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Certificate (translation)

PATENT OFFICE
JAPANESE GOVERNMENT

This is to certify that the annexed is a true copy of the following application as filed with this office.

Date of Application : 11 September 1997

Application Number : Patent Application No. 9-264972

Applicant : NGK Spark Plug Co.,Ltd.

Date 5 December 1997

Commissioner,
Patent Office

[Name of Document] Application for Patent
[Ref. No.] P6261NT
[Date of Submission] Year Month Day
Heisei 9 9 11
[Addressed to] Commissioner, Patent Office
[IPC] G01N 27/26
G01N 27/406
[Title of the Invention]
A Method and an apparatus for detecting the concentration of exhaust gas
[Number of claims] 10
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[Fee]
[Amount] Yen21,000.
[List of Documents]
[Name of document] Patent Specification 1
[Name of document] Drawings 1
[Name of document] Abstract 1
[Comprehensive Power Number] 9105125

NAME OF DOCUMENT SPECIFICATION

TITLE OF THE INVENTION

A method and an apparatus for detecting the concentration of exhaust gas.

CLAIMS

1. A method for detecting the concentration of exhaust gas using a gas sensor which detects the concentration of a specific component in a gas discharged from an internal combustion engine, the method comprising:

calibrating a zero point of a detection output of the gas sensor specifying the zero concentration of said specific component, based on a detection output of the gas sensor in atmosphere, and detects the concentration of said specific component based on the calibrated detection output.

2. A method for detecting the concentration of exhaust gas using a gas sensor which detects the concentration of a specific component in a gas discharged from an internal combustion engine, comprising:

calibrating the zero point of a detection output of the gas sensor specifying the zero concentration of the specific component, based on a detection output of the gas sensor obtained on cutting fuel supply to said internal combustion engine for setting the concentration of said specific component in the gas introduced into said gas

sensor substantially to zero or to substantially the same level as the atmosphere; and

detecting the concentration of said specific component based on the calibrated detection output.

3. A method for detecting the concentration of exhaust gases using a gas sensor which detects the concentration of a specific component in a gas discharged from an internal combustion engine, the method comprising:

calibrating the zero point of a detection output of the gas sensor specifying the zero concentration of the specific component, based on a detection output of the gas sensor obtained on setting a rich air-to-fuel ratio for said internal combustion engine to reduce said specific component and to set the concentration of said specific component in the gas introduced into said gas sensor substantially to zero or to substantially the same level as the atmosphere; and

detecting the concentration of said specific component based on the calibrated detection output.

4. The method as defined in any one of claims 1 to 3 wherein said gas sensor is a NOx sensor.

5. The method as defined in claim 4,

wherein said NOx sensor has first and second air gaps, first and second diffusion resistance units and first and second oxygen ion pump cells;

wherein said exhaust gases are diffused via said first diffusion resistance into said first gap, said first oxygen ion pump cell pumping out oxygen from said first gap so that oxygen in the gas diffused via said first diffusion resistance into said first gap will be of a specified oxygen concentration; and

wherein the gas having the specified oxygen concentration is diffused from said first gap via said second diffusion resistance into said second gap; NOx is decomposed in said second gap; said second oxygen ion pump cell pumping out dissociated oxygen ions; and the NOx concentration is detected from a current flowing in said second oxygen ion pump cell.

6. The method as defined in claim 4 or 5 wherein said NOx sensor is mounted downstream of a NOx occlusion catalyst and wherein said zero point is calibrated based on a detection output of said NOx sensor when an air-to-fuel ratio is temporarily set to a rich side for cleaning NOx occluded in said NOx occlusion catalyst.

7. A method for detecting the concentration of exhaust gases using a gas sensor which detects the concentration of a specific component in a gas discharged from an internal combustion engine, comprising:

driving the internal combustion engine under conditions which enable the concentration of said

specific component to be estimated or which render said concentration known;

calibrating a detection output of said gas sensor based on a detection output of said gas sensor under a driving condition for said engine; and

detecting the concentration of said specific component based on the calibrated detection output.

8. An apparatus for detecting the concentration of exhaust gases comprising:

a gas sensor detecting the concentration of a specific component in a gas discharged from an internal combustion engine;

driving condition setting means for setting driving conditions for the engine which enable the concentration of said specific component to be estimated or which render said concentration known; and

calibration means for calibrating a detection output of said gas sensor based on a detection output of said gas sensor under said driving conditions as set by said driving condition setting means.

9. An apparatus for detecting the concentration of exhaust gases comprising:

a NOx occlusion catalyst disposed in an exhaust pipe of an internal combustion engine;

a NOx sensor mounted downstream of said NOx occlusion

catalyst in the exhaust pipe to detect the NOx concentration in the exhaust gases;

driving condition setting means for transiently providing a rich air-to-fuel ratio for cleaning NOx occluded in said NOx occlusion catalyst; and

means for detecting a state of deterioration of said NOx occlusion catalyst based on changes in a detection output of said NOx sensor before and after setting the rich air-to-fuel ratio.

10. An apparatus for detecting the concentration of exhaust gases comprising:

a selectively NOx reducing catalyst arranged in an exhaust pipe of an internal combustion engine;

a NOx sensor mounted downstream of said catalyst in the exhaust pipe to detect the NOx concentration in the exhaust gases;

means for adding HC to exhaust gases of said internal combustion engine; and

means for detecting the state of deterioration of said catalyst based on changes in a detection output of said NOx sensor before and after HC addition.

DETAILED DESCRIPTION OF THE INVENTION

[0001]

[Technical Field of the Invention]

This invention relates to a method and apparatus for

detecting the exhaust gas concentration for measuring the concentration of harmful gas components contained in the exhaust gas from the internal combustion engine and, more particularly, to a method and apparatus for calibrating the zero point of an output of the NOx gas sensor.

[0002]

In coping with intensification of exhaust gas regulations, a sensor capable of measuring directly the concentration of harmful gas components contained in the exhaust gas, such as CO, HC, Nox. Thus, an oxide semiconductor type gas sensor, or a current limiting type gas sensor which uses an oxygen ion conductor, such as ZrO_2, are developing. The oxide semiconductor type gas sensor uses the relationship between the change of the electrical resistance and the amount of absorbed gas component to said oxide semiconductor. On the other hand, as a current limiting type gas sensor (Nox sensor), for example, a sensor that constructs the oxygen ion pump cell placed the electrode having the NOx decompose catalysis on the oxygen ion conductor, diffuses the gas controlled oxygen concentration in the space of facing said oxygen ion pump cell, decompose the Nox in said space, pumps the decomposed oxygen ion by an ion pumping cell, calculate the Nox gas concentration based on the current flowing in said oxygen ion pump cell, is proposed.

[PROBLEM TO BE SOLVED BY THE INVENTION]

An oxide semiconductor type gas sensor, however, suffers from poor reproducibility. On the other hand, in the current limiting type sensor, as a principle, there is raised a problem that the detection current flowing in the above-mentioned oxygen ion pumping cell is as very small as several μA. Moreover, since decomposition of harmful gas components (such as NOx) is controlled or suppressed by the catalytic action on the electrode surface, there is raised a problem that, on prolonged use, catalytic activity is changed to shift the zero point (detection output of the gas sensor specifying that the concentration of the pre-set component is substantially zero). Thus, none of the above enumerated gas sensor types is actually used as a sensor for prolonged time under significantly varying environment as in the case of a sensor mounted on an internal combustion engine, in particular the sensor mounted on an exhaust gas system of a vehicle.

[0004]

It is also an object of the present invention to provide a method and apparatus for detecting the exhaust gas concentration capable of measuring the gas concentration for prolonged time and, in particular, a method and apparatus which enable calibrating a zero point of the detection output of the NOx gas sensor.

[0005]

[MEANS TO SOLVE THE PROBLEM]

In order to solve the above problem, in the first means, the zero-point of the detection output of the gas sensor, indicating the zero concentration of a specific component, is calibrated based on the detected output of the gas sensor in atmosphere. The concentration of the specific component is detected based on the calibrated detection output. In the second means of the present invention, the supply of fuel to the internal combustion engine is cut to set the concentration of the specific component in the gas introduced into the gas sensor so as to be a level substantially equal to zero or to the atmosphere. Based on the detection output of the gas sensor on cutting the fuel supply, the zero point of the detection output of the gas sensor indicating the zero concentration of the specific component is calibrated.

[0006]

In the third means, the rich air-to-fuel ratio of the internal combustion engine is set to reduce the specific component in the exhaust gas to set the concentration of the specific component so as to be a level substantially equal to zero or to the atmosphere. In the fourth means, the internal combustion engine is driven under a condition in which the concentration of the specific component in

the gas discharged from the internal combustion engine can be estimated or is known. The detection output of the gas sensor is calibrated based on the detection output of the gas sensor under this operating condition. The concentration of the specific component is detected based on the detection output calibrated as above.

[0007]

In the fifth means, there is provided a gas sensor for detecting the concentration of a pre-set component in the gas discharged from the internal combustion engine. There is also provided calibration means for calibrating the detection output of the gas sensor based on the detection output of the gas sensor under the operating conditions as set by driving condition setting means. In the sixth means, there is provided a NOx occlusion type catalyst in an exhaust duct of the internal combustion engine. There is also provided driving condition setting means for transiently setting the rich air-to-fuel ratio atmosphere for cleaning NOx occluded in the NOx occlusion type catalyst. There is also provided means for detecting the state of deterioration of the NOx occlusion type catalyst based on changes in the detection output of the NOx gas sensor before and after setting the rich atmosphere.

[0008]

In the seventh means, there is provided a NOx selective reduction type catalyst arranged in an exhaust duct of an internal combustion engine. There is provided a NOx sensor mounted on a downstream side of the NOx selection reduction type catalyst for detecting the NOx concentration in the exhaust gas. There is also provided means for adding HC to the exhaust gas in the internal combustion engine. There is also provided means for detecting the state of deterioration of the NOx selective reduction type catalyst based on changes in the detection output of the NOx sensor before and after HC addition.

[0009]

The method for calibrating the detection output of the gas sensor based on the present invention is characterized in that the gas sensor is calibrated based on a detection output of the gas sensor under one of the driving conditions for the internal combustion engine which permits estimation of the concentration of the harmful exhaust gas components. In general, in an internal combustion engine of a vehicle having an electronically controlled fuel supply device, the fuel supply is cut when an output is not needed, as during deceleration. Thus, the concentration of the harmful gas components, such as NOx, HC or CO, is approximately of the same level as that in atmosphere. Conversely, the concentration of the harmful

gas components discharged from the internal combustion engine under the normal operating conditions is significantly higher than that in atmosphere. Thus, by calibrating the gas sensor during fuel cutting, the concentration of the harmful exhaust gas can be detected correctly even after prolonged use. Moreover, since it is the zero point of the detection output (offset) that is changed by prolonged use of the gas sensor, it is important to correct this zero point. For this purpose, the following would be pertinent. That is, the detection output upon fuel cutting is set to, for example, a level indicating the zero NOx gas concentration level.

[0010]

If the offset value of the detection output of the gas sensor (detection output in case of the zero concentration of the detected component, or the zero-point detection output) exhibits oxygen concentration dependency, that is if the offset value is changed with the oxygen concentration, the following is pertinent. Namely, if all offsets (for each value of the oxygen concentration) are corrected based on the value of the detection output at the time of fuel cutting for the known oxygen concentration and the concentration of the component to be detected. For example, if the difference between the initial value of an offset corresponding to

a pre-set oxygen concentration stored in the memory (OF1) and a detected output corresponding to the pre-set oxygen concentration at the time of fuel cutting (OF2), i.e., "OF1-OF2", is subtracted from an offset value OF[O2] for various values of the oxygen concentration stored in the memory, and the resulting value is stored in the memory as a new offset value OF[O2]. In the case of a sensor capable of measuring the oxygen concentration, the gas of the oxygen concentration substantially equal to that in atmosphere, that is the gas with the oxygen concentration of 20.9%, is supplied to the gas sensor to permit calibration of the sensitivity (gain). For example, by applying the method according to the present aspect to a NOx sensor as later explained, the sensitivity of the first oxygen pump current can be calibrated to permit correct measurement of the oxygen concentration after prolonged use.

[0011]

If the gas sensor is a NOx gas sensor, which is arranged downstream of the NOx occlusion catalyst, a spike of a rich atmosphere is introduced for reducing the occluded NOx. Since there is substantially no NOx emission at this timing, the zero point can be calibrated in the same way as described above. Moreover, comparison of detection outputs of the NOx sensor before and after insertion of

the rich-atmosphere spike permits detection of the catalyst deterioration (lowering of the NOx occlusion amount) without necessity of taking offset changes into account.

[0012]

[PREFERRED EMBODIMENTS OF THE INVENTION]

Now, a preferred embodiment in the present invention is explained. A desirable gas sensor of the present invention is a gas sensor capable of detecting the concentration of harmful components in the exhaust gases, such as combustible CO, HC and/or NOx components. As a CO sensor, a gas sensor employing an oxide semiconductor device, such as In_2O_3, may be used. As the HC sensor, such as gas sensor may be used which is provided with an oxygen pump element and an oxygen concentration cell element, both exposed to the detection gas, and which finds the concentration of the combustible gas components from the electric current values flowing in the oxygen pumping cell element when the electromotive force generated in the oxygen concentration cell element reaches a value not higher than a pre-set value. A gas sensor may be used which is provided with an oxygen pumping cell, an oxygen sensor cell and a combustible gas component detection unit formed of an oxide semiconductor. Also, a NOx sensor may be used which is provided with two sets of diffusion resistance

portions, oxygen ion pumping cells and gaps. The measurement principle of this NOx sensor is as follows:

[0013]

(1) Exhaust gases flow into the first gap via a first diffusion resistance portion having a diffusion resistance. (2) By the first oxygen ion pumping cell, oxygen in the first gap is sufficiently pumped out such as not to cause generally all NOx (or occasionally NOx) in the first gap to be decomposed (the oxygen partial pressure in the first gap is controlled by an output signal from a second diffusion resistance portion). (3) The gas in the first gap (concentration-controlled O2 gas or NOx gas) flows via second diffusion resistance portion into the second gap. (4) by the second oxygen ion pumping cell further pumping out oxygen, NOx in the second gap is decomposed into N2 and O2 gases. (5) Since there is a specific (roughly linear) relationship between the second oxygen pump current IP2 flowing in the second oxygen ion pumping cell and the NOx gas concentration, the NOx gas concentration in the exhaust gases can be detected by detecting Ip_2. (6) The oxygen concentration in the exhaust gases can be measured from the first oxygen pump current IP_1 flowing in the first oxygen ion pumping cell when the first oxygen ion pump current pumps out oxygen

from the first gap.

[0014]

A desirable method for using the above-mentioned NOx sensor in the exhaust gas cleaning system of a gasoline engine or a diesel engine is hereinafter explained. Referring to Fig.7(a), in an exhaust gas cleaning system of a gasoline engine (in particular a lean burn engine), an oxygen sensor (1), a NOx occlusion type three-way catalyst, an oxygen sensor (2) (the above elucidated NOx sensor used simultaneously as an oxygen sensor) are mounted in this order from the gasoline engine towards the downstream side. The oxygen sensor (1) is a sensor used for controlling the air-to-fuel ratio.. The fuel, air or the like supplied to an engine is controlled based on a detection output of this oxygen sensor (1). On the other hand, the NOx sensor used simultaneously as the oxygen sensor, arranged downstream of the NOx occlusion type three-way catalyst, is a sensor for detecting the NOx gas concentration for checking the operating state of the three-way catalyst and the state of deterioration thereof. The engine or the like is controlled based on the detection output of the NOx sensor. This NOx occlusion type three-way catalyst affords the NOx occlusion effect to the three-way catalyst and operates as a usual three-way catalyst with excessive air ratio $\lambda = 1$ (stoichiometric point) while

transiently storing NOx in the lean state and periodically introducing rich spikes for cleaning transiently stored NOx. In general, the material of the NOx occlusion type three-way catalyst is Pt added to with Ba etc. having the NOx occlusive effect.

[0015]

The above-mentioned NOx sensor, arranged downstream of the NOx occlusion type three-way catalyst, can be used for detecting the degree of deterioration of the NOx occlusion type three-way catalyst. That is, in introducing rich atmosphere spikes (preferably for about 3 seconds, air-to-fuel ratio of 14 to 14.5) for reducing NOx occluded in the NOx occlusion type three-way catalyst, the detection output of the NOx sensor is varied before and after the spike. If no deterioration has occurred, an output of the NOx sensor on reversion to the lean state after the spike becomes lower than that before the spike. Conversely, should there occur deterioration, NOx is not cleaned on returning from the spike to the lean state, with the NOx sensor output remaining at a high value. Thus, the degree of catalyst deterioration can be checked from changes in the NOx sensor output before and after rich spike. Since NOx is scarcely generated on spike insertion, the zero point of the NOx sensor can be calibrated.

[0016]

Referring to Fig.7(b), there are provided in a diesel engine exhaust gas cleaning system a light oil injection valve, a HC sensor, a NOx selective reduction catalyst and the above elucidated NOx sensor in this order. The light oil injection valve is used for injecting light oil as a HC source into the exhaust gases in the exhaust duct. The NOx selective reduction catalyst decomposes NOx into CO2 and H2O, using HC added by injection of light oil as a reducing agent, for cleaning NOx. The HC sensor is mounted upstream of the NOx selective reduction catalyst and performs the function of monitoring the HC concentration in the exhaust gases after light oil injection for performing feedback control of the amount of light oil injected into the exhaust gases. Moreover, the degree of deterioration of the NOx selective reduction catalyst can be detected based on output changes in the NOx sensor before and after HC addition. That is, with the catalyst having the capability of cleaning NOx, the NOx gas concentration downstream of the catalyst is lowered by HC addition to decrease the NOx sensor output, whereas, with the catalyst lowered in its cleaning capability, the NOx gas concentration is not lowered on HC addition, so that the output of the NOx sensor is not lowered.

[0017]

Fig.8 shows the control configuration of an exhaust

gas concentration detection system employing a NOx sensor according to an embodiment in the aspect D of the present invention. Referring to Fig.C8, this detection system has an internal combustion engine, a NOx sensor arranged downstream of the catalyst, an engine control unit (ECU) and a NOx sensor controller. The engine control unit sets the driving conditions for the internal combustion engine, such as the air-to-fuel ratio, and judges the catalyst deterioration. The NOx sensor controller includes means for controlling the NOx sensor, means for detecting and outputting the first oxygen pump current IP1 and the second oxygen pump current IP2 flowing in the NOx sensor, a memory for storing a map specifying the relation between the oxygen concentration and the IP2 offset value, an operation unit for reading out the IP2 offset from the memory and performing the operation based on an output of the detection means for outputting the results of the operation to the memory, and offset correction means supplied with a signal specifying the driving condition from the engine control unit and output signals from the IP1 and IP2 detection means for outputting an offset correction signal to the memory for storing a new offset value in the memory based on an output signal sent from the operating unit to the memory.

[0018]

The operation of this system is explained. The detection means of the NOx sensor controller detects the second oxygen pump current IP2 of the NOx sensor which the operation unit outputs to the memory. The engine control unit sets a driving condition of setting the NOx gas concentration in the exhaust gases to substantially zero or to substantially the same level as atmosphere. As an example, the driving condition is set to the fuel cut time condition, that is the NOx gas concentration equal to zero, with an oxygen concentration being 20.9%. If the signal specifying the above condition, outputted by the engine control unit, and the IP1, IP2 signals corresponding to the above condition outputted by the IP1 andIP2 detection means, the offset correction means outputs a pre-set offset correction signal to the memory for storing IP2 detected for the above condition in association with the oxygen concentration of 20.9%. This stored value serves as a calibrated new offset value of the NOx sensor detection output corresponding to the oxygen concentration of 20.9%. The operation unit reads out offset values corresponding to the oxygen concentrations stored in the memory to perform pre-set operations based on the read-out values, IP2 under the above condition and the offset value corresponding to the oxygen concentration of 20.9%, stored in the memory. Based on the results of the operation,

the offset values corresponding to the oxygen concentration are calibrated and stored in the memory. Such calibration of the detection output of the gas sensor is preferably performed periodically during the driving operation of the internal combustion engine. It may also be performed during idling.

[0019]

[Example]

An embodiment according to the aspect C of the present invention is explained. In the present embodiment, the NOx sensor having a structure shown in Fig.1 is used. The NOx sensor of Fig.1 includes a first oxygen ion pumping cell 6, having a pair of electrodes 6a, 6b provided on both sides of a solid electrolyte layer 5-1, an oxygen concentration measurement cell 7 having a pair of oxygen partial pressure detection electrodes 7a, 7b, provided on both sides of a solid electrolyte layer 5-2, and a second oxygen ion pumping cell 8 having a pair of electrodes 8a, 8b provided on the surfaces of a solid electrolyte layer 5-3 and a solid electrolyte layer 5-4, stacked in this order. Between the solid electrolyte layers 5-1, 5-2, 5-3 and 5-4 are formed insulating layers 11-1, 11-2 and 11-3, respectively. Between layers of the first oxygen ion pumping cell 6 and the oxygen concentration measurement cell 7 is defined the first measurement chamber (gap

portion) 2 by the left and right side insulating layer 11-1 and the upper and lower side solid electrolyte layers 5-1 and 5-2. Similarly, the second measurement chamber 4 (gap portion) is defined above the second oxygen ion pumping cell 8 by the insulating layer 11-3 and the solid electrolyte layers 5-3 and 5-4. Moreover, first diffusion hole 1 having a diffusion resistance (diffusion resistance portion) is provided on each side in the short side direction of the sensor (front and back sides in Fig.D1) on one side in the first measurement chamber 2. On the other side in the first measurement chamber 2 is formed with an opening of the second diffusion hole 3 (diffusion resistance portion) separated from the first diffusion holes 1. The second diffusion hole 3 is passed through the oxygen concentration measurement cell 7 and the solid electrolyte layer 5-3 to establish communication between the first and second measurement chambers 2 and 4 with a diffusion resistance.

[0020]

In the present sensor, electrodes 8a, 8b of porous metal (such as Pt or Rh alloys) are formed on the same surface of the solid electrolyte layer 5-4 making up the second oxygen ion pumping cell 8. Although the electrodes 8a, 8b are isolated from each other via the insulating layer 11-3, oxygen ions are conducted via the solid electrolyte

layer 5-4 to cause the second oxygen pump current Ip2 to flow by this oxygen ion conduction. The electrode 8b is prohibited by the solid electrolyte layer 5-4, insulating layer 11-3 and a lead (line) 8d from direct contact with the sensor atmosphere. Moreover, oxygen pumped out by the second oxygen ion pumping cell 8 can be led to outside via porous lead 8d having a diffusion resistance. Moreover, leads 8c (see Fig.2) and 8d (see Fig.2) are electrically connected to the electrodes 8a, 8b, while the lead 8d electrically connected to the outer electrode 8b of the second measurement chamber 4 is porous to permit oxygen ion diffusion. Thus, oxygen decomposed by the NOx gas and pumped from the electrode 8a to the electrode 8b is discharged via lead 8d. Fig.2 shows the planar cross-section taken along arrow line A in Fig.1. It is seen by referring to Fig.2 that the lead 8d is contacted with outside air (atmospheric air or ambient atmosphere of the measurement gas) for communication between outside air and the electrode 8b via a diffusion resistance.

[0021]

The principle of measurement of the NOx sensor shown in Fig. 1 is as explained in the column of the preferred embodiment. Specifically, controller terminals are electrically connected via leads to respective electrodes of the NOx sensor such that the electromotive force

corresponding to the oxygen concentration in the measurement gas, introduced by diffusion into the first measurement chamber 2 via the first diffusion holes 1, is generated across the electrodes 7a, 7b of the oxygen concentration measurement cell 7. The voltage applied across the first oxygen ion pumping cell 6 by the differential amplifier is controlled so that the voltage produced by this electromotive force will be constant (control by the controller may be digital control using a micro-computer or analog control). As excess oxygen is pumped out, the measurement gas having a pre-set oxygen concentration is diffused via the second diffusion hole 3 into the second measurement chamber 4 and the voltage is applied across the electrodes 8a, 8b of the second oxygen ion pumping cell 8 for further pumping out residual oxygen. NOx is decomposed into N2 and O2 by the catalytic action of the electrodes of Pt alloys or rhodium alloys. This O2 is converted into ions and transmitted in the solid electrolyte layer 5-4 of the second oxygen ion pumping cell 8 so that the current corresponding to the amount of the decomposed NOx gas flows across the electrodes 8a, 8b of the second oxygen ion pumping cell 8. The NOx gas concentration can be measured by measuring this IP2.

[0022]

With this NOx sensor, in which the electrode 8b

serving as an opposite side electrode with respect to the electrode 8a of the second oxygen ion pumping cell 8 in the second measurement chamber 4 is installed in the inside of the device (between layered solid electrolytes), the solid electrolyte layer 5-4 and the insulating layer 11-3 serve as protection means for the electrode 8b, with the lead portion 8d serving as diffusion resistance means to interrupt the electrode 8b from the atmosphere of the measurement gas (exhaust gases) to prevent it from direct contact with outside air. Moreover, pumped-out oxygen is pooled in the vicinity of the electrode 8b to stabilize the oxygen concentration around (in the vicinity of) the electrode 8b to stabilize the electromotive force generated across the paired electrodes 8a, 8b of the second oxygen ion pumping cell 8. Moreover, since the generated electromotive force is stabilized, the effective pump voltage (Vp2 - electromotive force) of the pump voltage Vp2 applied across the second oxygen ion pump cell 8 is stabilized to decrease oxygen concentration dependency in the measurement of the NOx concentration.

[0023]

[Manufacturing Example]

Next, a manufacturing method for a NOx sensor shown in Fig.1 is explained. Fig.3 is a layout view of the NOx sensor shown in Fig.1. Although the sheet and the paste

shown in Fig.3 are in the green state, the same reference numerals as those used for the NOx sensor shown in Fig.1 are used. The ZrO2 green sheet and the paste for the electrode are layered from upper left to lower left and then from upper right to lower right in Fig.3, dried and fired to form an integral sensor. The paste materials, such as insulating coat or electrodes, are layered by screen printing on a pre-set ZrO2 green sheet. The manufacturing example of the component parts such as ZrO2 green sheet is as described before.

[0024]

[Molding ZrO2 Sheet(5-1 to 5-2)]

ZrO2 powders were calcined in an atmospheric oven at 600for two hours. 30 kg of the calcined ZrO2 powders, 150 g of a dispersant and 10 kg of an organic binder were charged into a trommel along with 60 kg of balls. The resulting mass was mixed for about 50 hours for dispersion and added to with 4 kg of an organic binder dissolved in 10 kg of an organic solvent. The resulting mass was mixed for 20 hours to produce a slurry having a viscosity of 10 Pa·s. From this slurry, a ZrO2 green sheet about 0.4 mm thick was fabricated and dried at 100°C for one hour.

[0025]

[Paste for Printing]

(1) For first oxygen ion pump electrode 6a, an oxygen

partial pressure detection electrode (oxygen reference electrode b) 7b and second oxygen ion pump electrodes 8a, 8b: 20 g of platinum powders, 2.8 g of ZrO2 powders and a suitable quantity of the organic solvent were charged into a crusher (or a pot mill), mixed for four hours for dispersion and added to with 2 g of an organic binder dissolved in 20 g of the organic solvent. The resulting mass was added to with 5 g of a viscosity adjustment agent and mixed for four hours to produce a paste with a viscosity of the order of 150 Pa·s.

[0026]

(2) For first oxygen ion pump electrode 6b, oxygen partial pressure detection electrodes (oxygen reference electrode a) 7a: 19.8 g of platinum powders, 2.8 g of ZrO2 powders, 0.2 g of gold powders and a suitable quantity of the organic solvent were charged into a pulverizer (or a pot mill), mixed for four hours for dispersion and added to with 2 g of an organic binder dissolved in 20 g of the organic solvent. The resulting mass was added to with 5 g of a viscosity adjustment agent and mixed for four hours to produce a paste with a viscosity of the order of 150 Pa·s.

[0027]

(3) For insulating coats and protective coats: 50 g of alumina powders and a suitable amount of the organic solvent were charged into a pulverizer (or a pot mill) and

mixed for 12 hours for dissolution. The resulting mass was added to with 20 g of a viscosity adjustment agent and mixed for three hours to fabricate a paste with a viscosity of the order of 100 Pa·s.

[0028]

(4) For Pt-containing Porous Materials (Lead Wires): 10 g of alumina, 1.5 g of platinum powders, 2.5 g of an organic binder and 20 g of an organic solvent were charged into a pulverizer 9 or a pot mill) and mixed for four hours. The resulting mass was added to with 10 g of a viscosity adjustment agent and mixed for four hours to fabricate a paste with a viscosity of the order of 100 Pa·s.

[0029]

(5) For first diffusion hole 1: 10 g of alumina powders having an average grain size of about 2μm, 2 g of an organic binder and 20 g of an organic solvent were charged into a pulverizer (or a pot mill) and mixed for four hours. The resulting mass was added to with 10 g of a viscosity adjustment agent and mixed for four hours to fabricate a paste with a viscosity of the order of 400 Pa·s.

[0030]

(6) For carbon Coat: 4 g of carbon powders, 2 g of an organic binder and 40 g of an organic solvent were charged into a pulverizer (or a pot mill) and mixed for dispersion. The resulting mass was added to with 5 g of a a viscosity

adjustment agent and mixed for four hours to fabricate a paste. By forming the carbon coat by printing, electrical contact between electrodes, for example, can be eliminated. The carbon coat is used for forming first and second measurement chambers. Since carbon is burned off during firing, there is no carbon coat layer in the sintered body.

[0031]

[Pellet]

For Second Diffusion Hole 3: 20 g of alumina powders, with a mean particle size of about 2μm, 8g of an organic binder and 20 g of an organic solvent were charged into a pulverizer (or a pot mill) and mixed for one hour. The resulting mass was granulated and pressed by a metal mold press under a pressure of approximately 2 t/cm^2 to fabricate a press-molded product (in the green state) in the from of a column 0.8 mm thick with a diameter of 1.3mm. This press-molded product in the green state was inserted into a pre-set point of green sheets of the second and third ZrO2 green sheets and press-bonded together. The resulting product was then fired to form the second diffusion hole 3 in the gas sensor.

[0032]

[Means for Laminating ZrO2]

After pressure bonding the second and third layers, a portion to be passed through by the second diffusion hole

3 is punched. After this punching, a green columnar-shaped molded product, which serves as the second diffusion hole 3, is embedded, and the third to fourth layers of ZrO2 green sheets are pressure-bonded together under a force of pressure of 5 kg/cm^2 for a pressing time duration of one minute.

[0033]

[Binder Removal and Firing]

The pressure-bonded molded product was fired at 1500°C for one hour after removal of the binder at 400°C for two hours.

[0034]

[Use Example]

The NOx sensor, thus produced, having a structure as shown in Fig.1, was mounted on an actual apparatus and put to a durability test continuing for 500 hours. The structure of the NOx gas concentration sensor is like that shown in Fig.8, while the mounting position of the NOx gas sensor is like that shown in Fig.7a. The controller controlling the NOx gas sensor has a memory in which to store the gain value ((standard NOx gas concentration - 0)/(generated current volume - offset)) of a detection output of the NOx gas sensor as set using a model gas evaluation device as later explained (second oxygen pump current) . In particular, the offset values corresponding

to various oxygen concentration values from the oxygen concentration of 0% to 20.9% (21%) are stored in the memory for cancelling its oxygen concentration dependency. In this manner, optimum offset values are read out based on the oxygen concentration as found from the first oxygen pump current for setting optimum offset values used for calculating the NOx gas concentration.

[0035]

Two sets of the controllers and the NOx sensors were prepared and initial characteristics of NOx gas sensors thereof were measured on a model gas evaluation device. The controllers were adjusted so that, when the analyzer output indicated zero NOx gas concentration, the controller detection output corresponding to the second oxygen pump current will be equal to zero. These NOx gas sensors were then mounted on an exhaust pipe of a gasoline engine with a displacement of 3000 cc, and a 500-hour durability test was conducted in a mode shown in Fig.C4, during which the NOx gas sensors were controlled by the respective controllers (numerals affixed to the indication of the number of revolutions depict relative opening degree of the accelerators). In one of the controllers, the correction method of the embodiment was executed to calibrate the offset (zero point) during fuel cut for the durability mode. In the other controller, the

zero point was not calibrated. The calibration method by the former controller is as follows:

[0036]

That is, referring to Fig.5, when the fuel cut signal output from the engine control unit (ECU) of the gasoline engine is entered, the value of the controller detection output, proportionate to the second oxygen pump current, is stored as an offset value (OF2) corresponding to O2=20.9%. The offset value (OF1) in the memory, corresponding to O2=20.9%, is read out to find the difference between OF1 and OF2. The resulting "OF1-OF2" is subtracted from the offset value OF[O2] corresponding to each oxygen concentration stored in the memory to give a value (OF[O2]-(OF1-OF2)) which is stored in the memory as a calibrated new offset value OF[O2].

[0037]

Referring to the results of the durability test, shown in Fig.6, the detection output of the NOx gas concentration of the controller of the system according to the calibrated embodiment indicated substantially zero change after the durability test continued for 500 hours. Conversely, the output was increased by approximately 400 ppm for the system of the comparative example for which no calibration was carried out.

[0038]

[EFFECTS OF THE INVENTION]

According to the present invention, the internal combustion engine is driven under a condition in which the concentration of the measurement component can be estimated or is known. The shift of the detection output of the gas sensor after durable use is cancelled by calibrating the gas sensor under this operating condition. Thus, the concentration of the measurement component can be detected correctly. As a gas sensor applicable of the present invention, Nox sensor as well as HC and CO sensor are acceptable. Actually, in a sensor capable of measuring the oxygen concentration, calibration of the response for oxygen concentration can be performed, because the oxygen concentration is not zero but the gas of 20.9% of oxygen concentration is introduced, when, for example, the fuel supply is cut. Also when the fuel supply is cut and the air-to-flow ratio is rich, the calibration of the present invention can be performed. Thus, a special operating condition for the calibration is not necessary. Especially, the present invention is applied to Nox gas sensor, the correct measurement of Nox gas concentration in the range of ppm order can be performed for prolonged time(claim 4). In particular, when the NOx sensor for detecting Nox concentration in a gas discharged from an internal combustion engine, is mounted downstream of a NOx occlusion

catalyst, said calibration can be performed using the mode in which an air-to-fuel ratio is set to a rich side for reducing NOx occluded in said NOx occlusion catalyst(claim 6). And also, a state of deterioration of said NOx occlusion catalyst can be detected(claim 9). According to the invention of claim 10, the state of deterioration of a selectively NOx reducing catalyst arranged in an exhaust pipe of the system using a diesel engine incapable of setting a rich air-to-flow ratio, can be detected.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig.1 is a schematic view for illustrating the structure of a NOx gas sensor employed in an embodiment of the present invention.

Fig.2 illustrates the cross-section indicated by arrow A in Fig.1.

Fig.3 illustrates the layout of a NOx gas sensor shown in Fig.C1.

Fig.4 illustrates a durability test mode conducted using a NOx gas sensor shown in Fig.1.

Fig.5 illustrates a method for calibration for detection output of the NOx gas sensor according to an embodiment of the present invention.

Fig.6 illustrates the results of the durability test wherein a square plot and a triangular plot indicate data of an embodiment and a comparative example.

Figs.7(a) and 7(b) illustrate an exhaust gas concentration detection apparatus employing a NOx gas sensor according to an embodiment of the present invention wherein (a) illustrates an exhaust gas cleaning system of a gasoline engine (especially a lean-burn engine) and (b) illustrates an exhaust gas concentration detection apparatus applied to an exhaust gas cleaning system of a diesel engine.

Fig.8 illustrates an exhaust gas concentration detection system employing a NOx gas sensor according to an embodiment of the present invention.

EXPLANATION OF THE REFERENCE NUMERALS

1:first diffusion holes

2:a first measurement chamber

3:second diffusion holes

4:a second measurement chamber

5-1, ---, 5-4:a solid electrolyte layer

6:a first oxygen ion pumping cell

6a, 6b:electrode

6c:lead

7:oxygen concentration measurement cell

7a,7b:electrode

8:second oxygen ion pumping cell

8a,8b:electrode

8c,8d:lead

11-1, ---, 11-3:insulating layer

FIG. 1

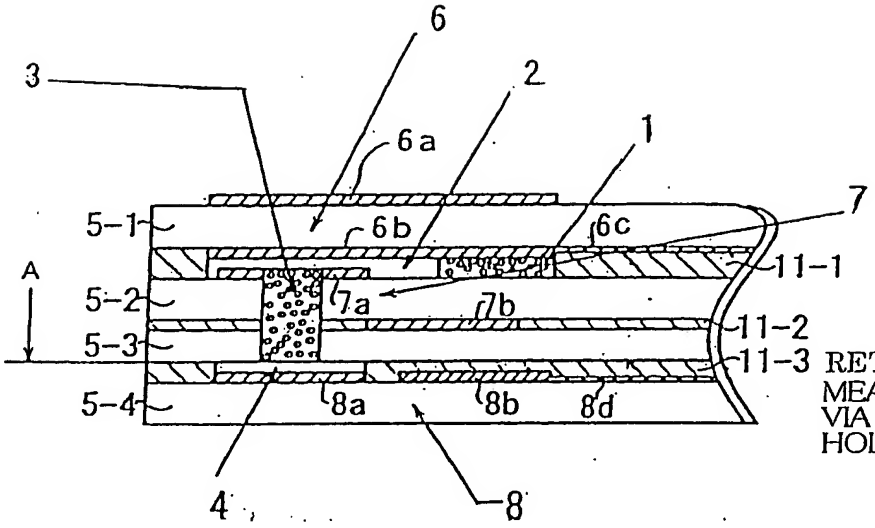
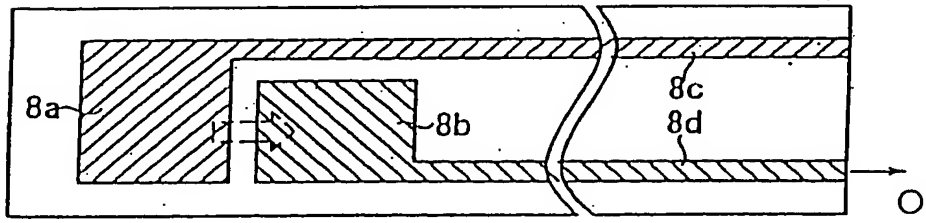


FIG. 2



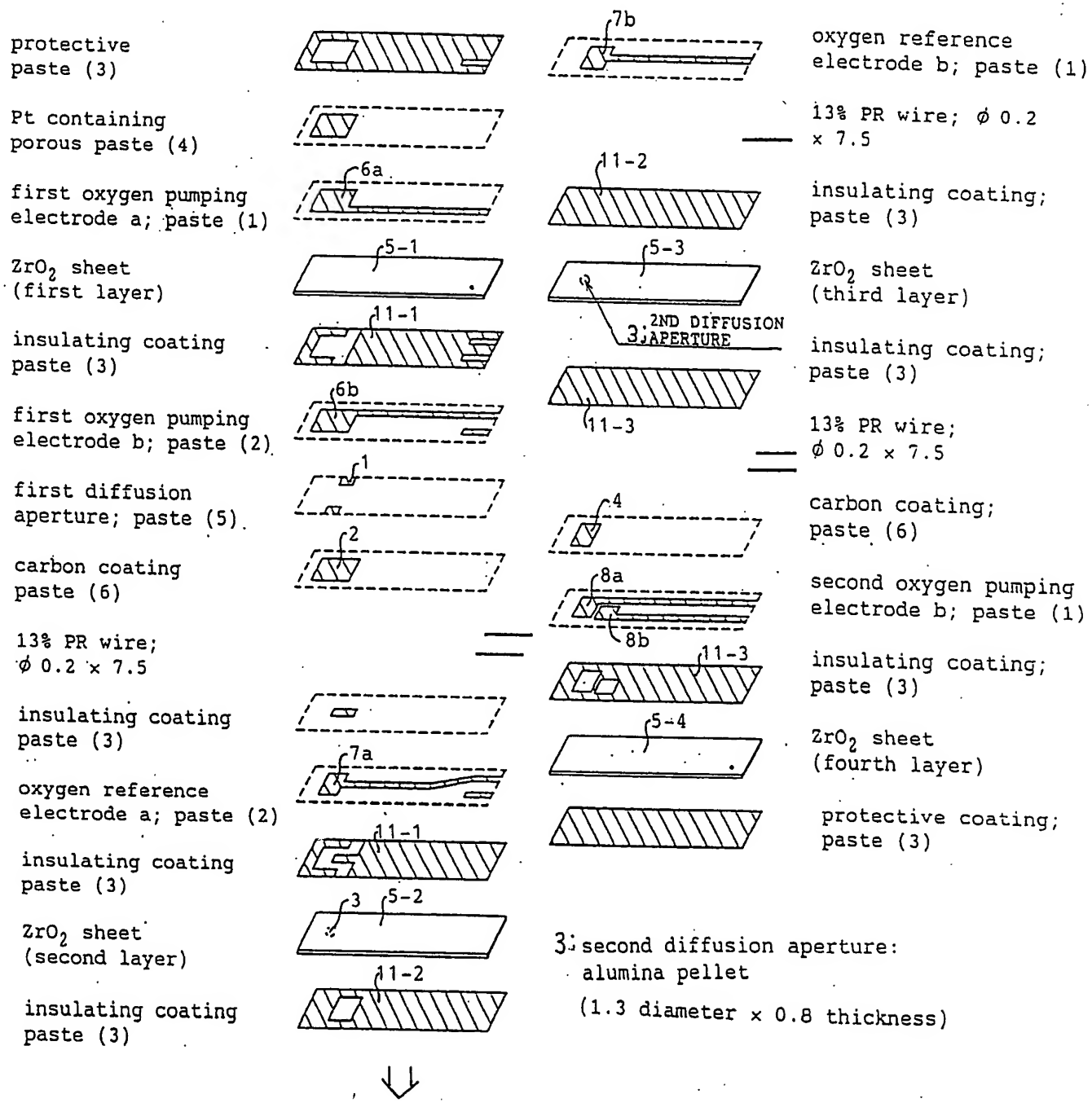


FIG. 3

FIG. 4

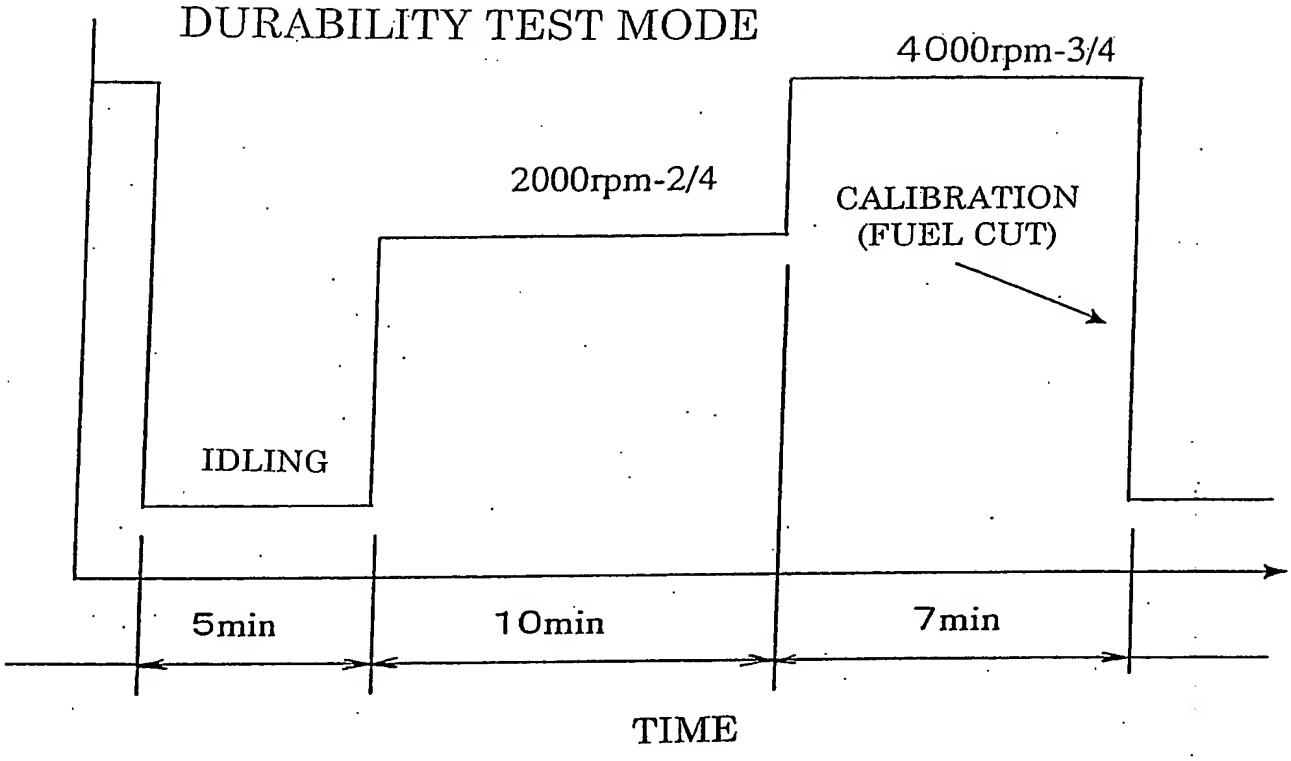


FIG. 5

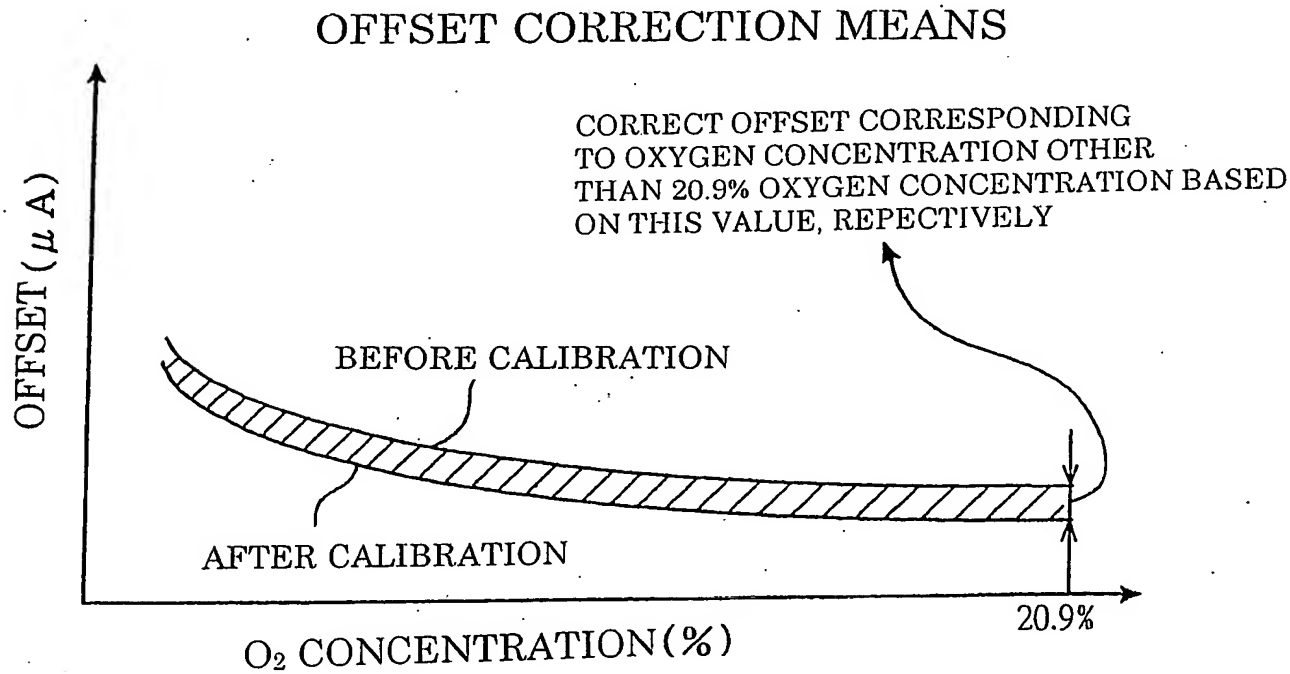


FIG. 6

DURABILITY TEST RESULT

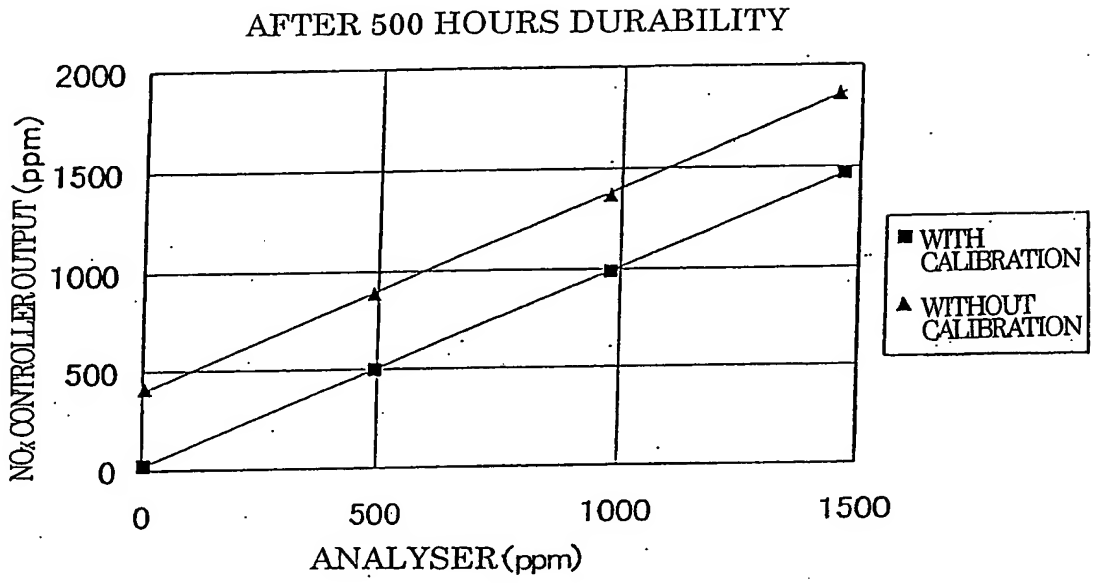


FIG. 7

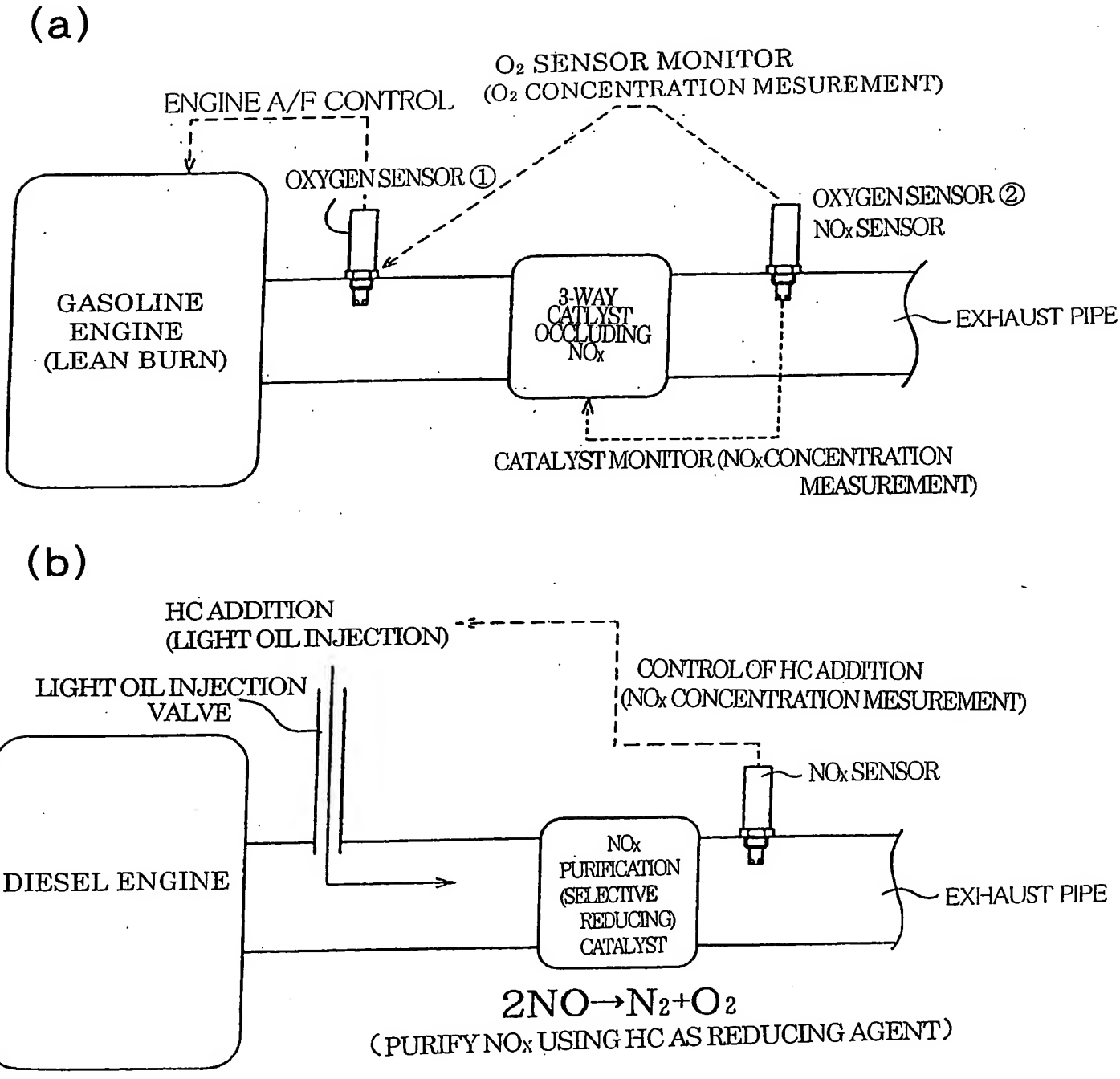
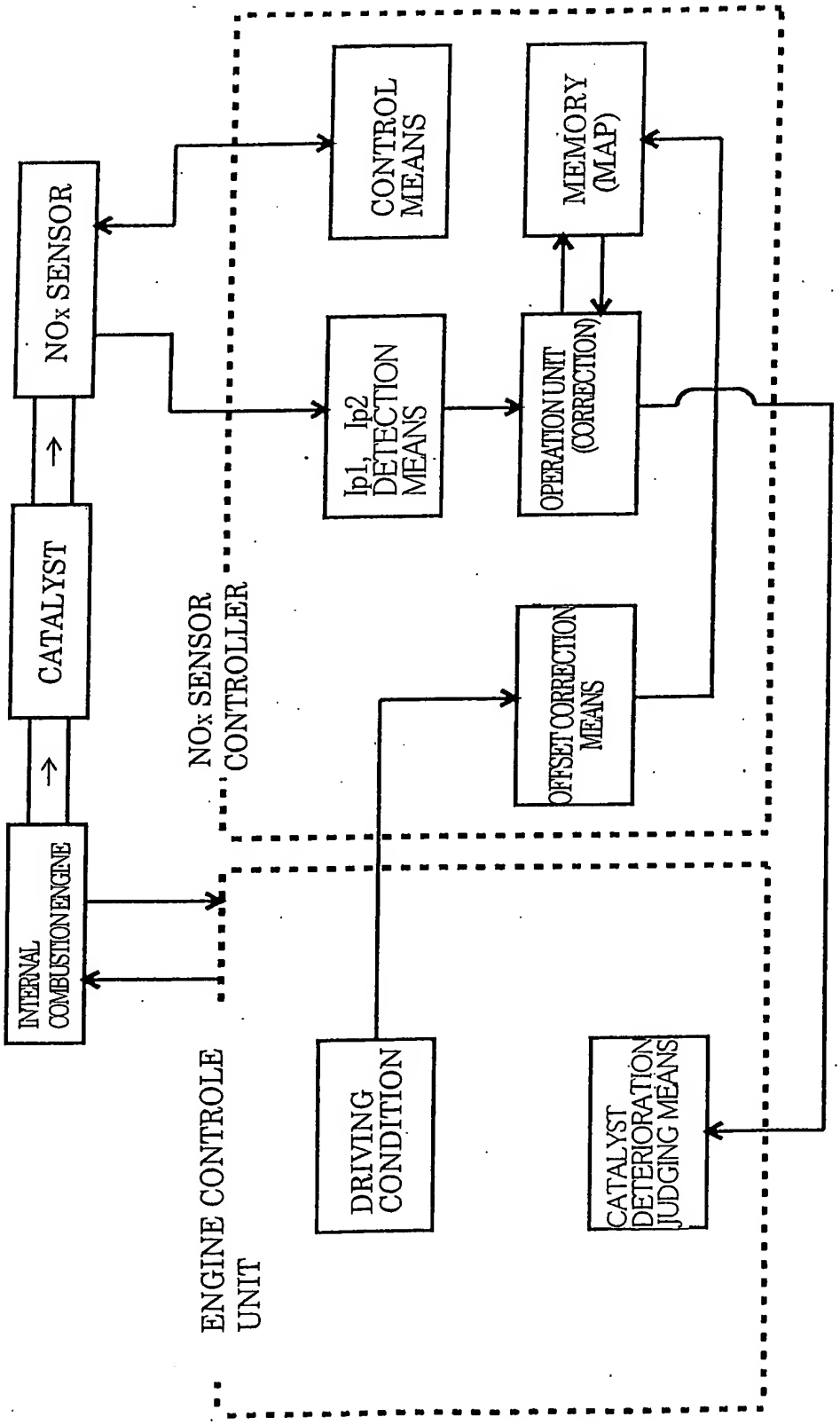


FIG. 8



NAME OF DOCUMENT ABSTRACT

SUMMARY

[Object]

to provide a method and apparatus for detecting the exhaust gas concentration capable of measuring the gas concentration for prolonged time with high accuracy.

[Means for Solution]

In the detection method of the exhaust gas concentration by using the gas sensor for detecting a concentration of a certain component in the gas, the zero-point of the detection output of the gas sensor, indicating the zero concentration of a specific component, is calibrated based on the detected output of the gas sensor in atmosphere. The concentration of the specific component is detected based on the calibrated detection output.

[Selected Drawing]

Figure 8